

# Statistical Thermodynamics in Chemistry and Biology

## 8. Laboratory conditions and free energies

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# Switch from maximum entropy to minimum free energy

$S(U, V, N)$

- ▶ The boundaries are controlled by the internal energy,  $U$ , volume,  $V$ , and number of particles,  $N$ .
- ▶ Reasonable properties to control experimentally.
- ▶ Equilibrium principle: **entropy is maximized**

$U(S, V, N)$

- ▶ The boundaries are controlled by the entropy,  $S$ , volume,  $V$ , and number of particles,  $N$ .
- ▶ The entropy is difficult(impossible) to control experimentally.

## Introduce new independent variables

- ▶ It would be natural to use *temperature*, *pressure*, and *chemical potential* as independent variables.
- ▶ More convenient to control experimentally (c.f. biological systems)
- ▶ New thermodynamics quantities: enthalpy, free energies
- ▶ New equilibrium principle: **minimum free energy**

# Helmholtz Free Energy

- ▶ Constant **temperature**,  $T$ , volume,  $V$ , and number of particles,  $N$ .
- ▶ Heat is transferred to and from a heat bath to keep the temperature constant.
- ▶ One step back: treat the *system* and the *bath* as a *combined system*,  $S_{\text{combined}}(U, V, N)$ :

$$dS_{\text{combined}} = dS_{\text{system}} + dS_{\text{bath}} \geq 0$$

where  $\dots \geq 0$  denotes that  $S$  is maximized.

- ▶ The combined system is **isolated**:

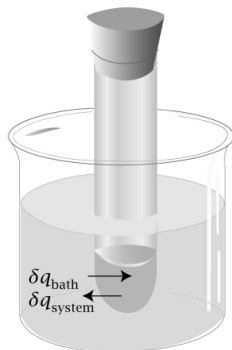
$$dU_{\text{combined}} = dU_{\text{bath}} + dU_{\text{system}} = 0$$

- ▶ Use the fundamental equation for  $dS$ :

$$dS_{\text{bath}} = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN = \frac{1}{T}dU_{\text{bath}}$$

for a bath where  $V$  and  $N$  are constant.

Constant Volume



# The Helmholtz free energy

## Part 2

- ▶ Combining the last two equations,

$$dS_{\text{bath}} = -\frac{dU_{\text{system}}}{T}$$

which leads to

$$dS_{\text{system}} - \frac{dU_{\text{system}}}{T} \geq 0 \quad \Rightarrow \quad dU_{\text{system}} - TdS_{\text{system}} \leq 0$$

- ▶ Condition for equilibrium in terms of the **system** (test tube) alone.
- ▶ Define a quantity,  $F$  (sometimes  $A$ ), **Helmholtz free energy**

$$F = U - TS$$

- ▶ Its differential is

$$dF = dU - TdS - SdT$$

and at **constant temperature**, the condition above is obtained for  $dF$ ,

$$dF = dU - TdS$$

- ▶ The Helmholtz free energy is **minimized** at equilibrium:  $dF = 0$ .

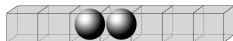
# A model for dimerization

- ▶ Two particles,  $N = 2$ ,  $V$  lattice points (constant volume), and constant temperature.
- ▶ Minimize Helmholtz free energy,  $F$  (actually, compare  $F_{\text{dimer}}$  and  $F_{\text{monomer}}$ ).
- ▶ “Bond energy” given:  $U = -\varepsilon$  ( $\varepsilon > 0$ )
- ▶ **Dimer** case: the multiplicity becomes

$$W_{\text{dimer}} = V - 1$$

- ▶ The Helmholtz free energy:

$$F_{\text{dimer}} = U_{\text{dimer}} - TS_{\text{dimer}} = -\varepsilon - k_B T \ln(V - 1)$$



# A model for dimerization

## Part 2

- **Monomer** case: the multiplicity becomes

$$W_{\text{monomer}} = W_{\text{total}} - W_{\text{dimer}} = \frac{V!}{2!(V-2)!} - (V-1) = \left(\frac{V}{2} - 1\right)(V-1)$$

- The Helmholtz free energy:

$$\begin{aligned} F_{\text{monomer}} &= U_{\text{monomer}} - TS_{\text{monomer}} = -TS_{\text{monomer}} \\ &= -k_B T \ln \left( \left( \frac{V}{2} - 1 \right) (V-1) \right) \end{aligned}$$

- Recapitulate the Helmholtz free energy for the dimer:

$$F_{\text{dimer}} = U_{\text{dimer}} - TS_{\text{dimer}} = -\varepsilon - k_B T \ln(V-1)$$

- Which state (dimer or monomer) dominates? Which has the lowest free energy? The **temperature** governs! The dimer is stable at 0 K, but at some temperature the monomer state will become stable.

# Fundamental equation for the Helmholtz free energy

- ▶ Multivariate calculus again for  $F(T, V, N)$ :

$$dF = d(U - TS) = dU - TdS - SdT$$

- ▶ Use the equation for  $dU$ :

$$\begin{aligned} dF &= \left( TdS - pdV + \sum_{j=1}^m \mu_j dN_j \right) - TdS - SdT \\ &= -SdT - pdV + \sum_{j=1}^m \mu_j dN_j \end{aligned}$$

- ▶ Compare  $U(S, V, N)$  and  $F(T, V, N)$ .

# Fundamental equation for the Helmholtz free energy

## Part 2

- We can also write  $dF$  as

$$dF = \left( \frac{\partial F}{\partial T} \right)_{V, \mathbf{N}} dT + \left( \frac{\partial F}{\partial V} \right)_{T, \mathbf{N}} dV + \sum_{j=1}^m \left( \frac{\partial F}{\partial N_j} \right)_{T, V, N_{i \neq j}} dN_j$$

and we get the following relations:

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V, \mathbf{N}} ; \quad p = - \left( \frac{\partial F}{\partial V} \right)_{T, \mathbf{N}} ; \quad \mu_j = \left( \frac{\partial F}{\partial N_j} \right)_{T, V, N_{i \neq j}}$$

- We will not go into Legendre transforms in detail. See Appendix F.



# The enthalpy, $H$

- ▶ The enthalpy  $H(S, p, N)$ , (c.f.  $U(S, V, N)$ ,  $F(T, V, N)$ )
- ▶ “Standard procedure”:

$$H = H(S, p, N) = U + pV$$

- ▶ Differentiate:

$$dH = dU + pdV + Vdp$$

- ▶ Substitute with the expression for  $dU$ :

$$dH = \left( TdS - pdV + \sum_{j=1}^m \mu_j dN_j \right) + pdV + Vdp$$

$$dH = TdS + Vdp + \sum_{j=1}^m \mu_j dN_j$$

- ▶ Why **not**  $H = U - pV$ ?

# The Gibbs free energy, $G$

- ▶ The Gibbs free energy,  $G(T, p, N)$  (c.f.  $H(S, p, N)$ ,  $F(T, V, N)$ )
- ▶ Standard procedure:

$$G = H - TS$$

- ▶ Differentiate:

$$dG = dH - TdS - SdT$$

- ▶ Substitute with the expression for  $dH$ :

$$dG = \left( TdS + Vdp + \sum_{j=1}^m \mu_j dN_j \right) - TdS - SdT$$

$$dG = -SdT + Vdp + \sum_{j=1}^m \mu_j dN_j$$

- ▶ Many other possibilities than  $S(U, V, N)$ ,  $U(S, V, N)$ ,  $F(T, V, N)$ ,  $H(S, p, N)$ , and  $G(T, p, N)$ ?

Yes, but most of them are not very useful (see table 8.1 for a helpful list)

# Heat capacity, $C_p$

- ▶ We regard  $H(S, p, N)$ ,

$$dH = d(U + pV) = dU + pdV + Vdp = \delta q + \delta w + pdV + Vdp$$

- ▶ Quasistatic processes:  $\delta w = -pdV$ . Constant pressure:  $dp = 0$ . Gives:

$$dH = \delta q$$

- ▶ The **heat capacity,  $C_p$**  is defined as,

$$C_p = \left( \frac{\delta q}{dT} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p$$

- ▶ Analogous to  $C_V$ .

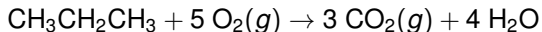
# Thermochemistry

- ▶ The enthalpy of a molecule is regarded as a sum of **enthalpies for covalent bonds**.
- ▶ The enthalpy for a chemical reaction is defined as

$$\Delta\Delta H_{\text{total}} = \Delta H_{\text{reac}} - \Delta H_{\text{prod}}$$

which is the difference between the formation enthalpy of the reactants and products.

- ▶ Best explained with example 8.6 (burning propane):



- ▶ Use bond enthalpies (in kJ/mol) from Table 8.3. C-C: 347, C-H: 414, O=O: 499, C=O (in CO<sub>2</sub>): 799, O-H: 460.
- ▶ Results in

$$\begin{aligned}\Delta\Delta H_{\text{total}} &= (8 \times 460 + 6 \times 799) - (2 \times 347 + 8 \times 414 + 5 \times 499) \text{ kJ/mol} \\ &= -1974 \text{ kJ/mol}\end{aligned}$$

# Ensembles

See chapter 10, pages 188-189

- ▶ In this chapter we have considered systems in which  $(T, V, N)$  is constant. This is called the **canonical ensemble**.
- ▶ An ensemble has the following meaning:  
The collection of all microstates of the system that fulfill the macroscopic constraints (e.g.  $(T, V, N)$ )
- ▶ Examples of ensembles:
  - canonical ensemble  $(T, V, N)$
  - isobaric-isothermal ensemble  $(T, p, N)$
  - grand canonical ensemble  $(T, V, \mu)$  (see chapter 28)
  - microcanonical ensemble  $(U, V, N)$

# Summary

- ▶ Introduced **Helmholtz free energy**, **enthalpy** and **Gibbs free energy**.
- ▶ General procedure for introducing new **state functions**.
- ▶ Minimization principle for free energies.
- ▶ Model system for dimerization (first system where we minimize/compare free energies).

## E8.1 (Exam Dec. 2008:4)

### A lattice model for dimerization

Construct a lattice model for dimerization on a surface. The surface consists of quadratic lattice with  $A = L^2$  sites. The two identical and indistinguishable molecules (monomers) are bound to the surface. The molecule-surface interaction energy is  $\varepsilon_0$ , and the dimer binding energy is  $\varepsilon$ .

a) Give an expression for the Helmholtz free energy of dimerization,

$$\Delta F = F_{\text{dimer}} - F_{\text{monomer}}$$

b) What is the condition for dimerization to occur? In particular, what is the condition for  $\varepsilon$ ? Will dimerization be more likely at higher or lower temperatures?

c) Briefly described, *cooperativity* is the effect of binding to a surface or an enzyme when already a neighbour molecule is bound. For example, an oxygen molecule binds easier to hemoglobin when already one or several oxygen molecules are bound. Suggest how  $\varepsilon_0$  may be modified to include cooperativity in this model?